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Influence of magnesia in the infiltration of magnesia-spinel refractory bricks by different clinkers

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Geraldo Eduardo Gonçalves
Doutor,
Consultor do Centro de Pesquisas da Magnesita,
Belo Horizonte - Minas Gerais - Brasil
ggoncalves@magnesita.com

Graziella Rajão Cota Pacheco
Mestre,
Pesquisadora Sênior do Centro de Pesquisas da Magnesita,
Belo Horizonte - Minas Gerais - Brasil
graziella.rajao@magnesita.com

Modestino Alves de Moura Brito
Mestre,
Diretor do Centro de Pesquisas da Magnesita,
Belo Horizonte - Minas Gerais - Brasil
modestino@magnesita.com

Sérgio Luiz Cabral da Silva
Doutor,
Professor do Departamento de Engenharia Química da UFMG e Pesquisador Especialista do Centro de Pesquisas da Magnesita,
Belo Horizonte - Minas Gerais - Brasil
ssilva@magnesita.com

Vanessa de Freitas Cunha Lins
Doutor,
Professor do Departamento de Engenharia Química da UFMG,
Belo Horizonte -Minas Gerais -Brasil
vlins@deq.ufmg.br

Abstract

In cement production, which involves the production of cement clinker in rotary kilns, the main refractories used are magnesia-spinel bricks. These bricks may suffer infiltration by the clinker liquid phase, resulting in the corrosion of the spinel and the formation of low refractoriness mineralogical phases, such as the Q phase ($C_{20}A_{13}M_3S_3$), which compromises refractory performance. Thus, the aim of this work is to correlate the infiltration resistance of magnesia-spinel bricks made from different grades of magnesia by clinker collected in three different cement plants (A, B and C). The purity of magnesia, besides its physical properties, strongly influences the properties and the infiltration resistance of magnesia-spinel bricks; as such the use of high grade magnesia is essential for producing high performance refractories.

Keywords: Magnesia-spinel refractory brick; infiltration; clinker.

1. Introduction

The refractory materials include a wide range of oxide or mixture of oxides as well as other materials such as carbon, carbides, nitrides and borides. These materials exhibit superior physicochemical, thermodynamic and structural properties at elevated temperatures, such as a high melting point/refractoriness, resistance to chemical corrosion in an aggressive media, and structural stability (Liu *et al*., 2013).

The largest customer of the refractory industry is the steel industry, with 70% of the total world production, followed by cement and lime industries, with 7% of refractory production for these markets (Mourão, 2007). In the cement industry, the manufacture of Portland cement involves the steps of grinding the raw material (clay, limestone, bauxite, etc.), homogenization of the raw meal, clinkerization (sintering of the raw meal forming clinker) in rotary kilns, cooling, and grinding of clinker. The clinker produced has a typical composition of 67% CaO, 22% SiO_2, 5% Al_2O_3, 3% Fe_2O_3 and 3% other components, and four main mineralogical phases identified as C_3S ($3CaO.SiO_2$), C_2S ($2CaO.SiO_2$), C_3A ($3CaO.Al_2O_3$) and C_4AF ($4CaO.Al_2O_3.Fe_2O_3$) (Taylor, 1990).

Magnesia-spinel refractory is widely used in upper transition, burning and lower transition zones of rotary kilns in the clinker production and replaced the magnesia-chromite refractory due to environmental issues relating to the formation of Cr^{6+}, which is considered toxic (Szczerba *et al.*, 2007). These refractories have two main mineralogical phases: periclase (MgO) and spinel ($MgO.Al_2O_3$ or MA).

The spinel is traditionally added between 5 and 30% by weight to magnesia-spinel refractory, which corresponds to an alumina content between 3 and 20wt.%, approximately. According to Ghosh *et al.* (2004), among the studied concentrations of 10, 20 and 30wt.% of spinel added to the magnesia-spinel refractory matrix, there is a content of 20% optimized properties, such as refractoriness under load, thermal shock resistance and hot modulus of rupture.

Literature is extensive with respect to the study of the properties of magnesia-spinel refractory (Szczerba *et al.*, 2007; Ghosh *et al.*, 2004; Grasset-Bourdel *et al.*, 2012; Grasset-Bourdel *et al.*, 2013; Aksel *et al.*, 2002; Aksel *et al.*, 2004a; Aksel *et al.*, 2004b; Sarkar *et al.*, 2003; and Aksel *et al.*, 2004c), specially the thermal shock resistance. Due to the difference between the thermal expansion coefficient of periclase ($13\text{-}15 \times 10^{-6}$ °C^{-1}) and spinel ($8\text{-}9 \times 10^{-6}$ °C^{-1}) (Szczerba *et al.*, 2007), radial micro cracks are generated around spinel grains during the cooling of the refractory in the heat treatment step, thereby increasing its resistance to thermal shock.

Magnesia-spinel refractory exhibits excellent performance in most rotary kilns. However, premature wear can occur due to fluctuations in operating conditions. The main wear mechanisms are infiltration by volatile compounds, infiltration by the clinker liquid phase and mechanical stress.

In the case of infiltration by the clinker liquid phase, CaO from C_3S peritectic decomposition ($C_3S \rightarrow C_2S + CaO$ at 1250 °C) reacts with Al_2O_3 of the spinel forming mayenite phase ($C_{12}A_7$) in the temperature range between 1000°C and 1350°C, with the probable mechanism indicated by Equation 1 (Gonçalves and Bittencourt, 2003; Wajdowicz *et al.*, 2011):

$$7\ MA_{(brick)} + 12\ C_3S_{(clinker)} + \text{liquid phase} \rightarrow C_{12}A_7 + 7\ M + 12\ C_2S + \text{liquid phase} \qquad (1)$$

The mayenite is an intermediate phase, which, in the absence of SO_3, leads to the formation of the Q phase ($C_{20}A_{13}M_3Si_3$ or $Ca_{20}Al_{26}Mg_3Si3O_{68}$) between 1300 °C and 1400°C, with probable mechanism indicated by Equation 2 (Gonçalves and Bittencourt, 2003; Wajdowicz *et al.*, 2011):

$$C_{12}A_7 + 3\ MA_{(brick)} + 3\ C_2S_{(clinker)} + 2\ C_{(clinker)} + 3\ A_{(brick)} + \text{liquid phase} \rightarrow C_{20}A_{13}M_3S_3 + \text{liquid phase} \qquad (2)$$

Mayenite and the Q phase are low refractoriness phases, which compromise the performance of the refractory in the rotary kilns. Rodríguez *et al.* (2012) reported the excellent resistance to the clinker of bricks based on sintered magnesia and electrofused magnesia-calcium zirconate ($MgO\text{-}CaZrO_3$) using spinels of magnesium aluminate ($MgAl_2O_4$) and hercynite ($FeAl_2O_4$) in the refractory matrix.

According to our knowledge, the relation between refractory raw materials and infiltration resistance is not found in literature. Liu *et al.* (2014) investigated the composition and microstructure of a periclase–composite spinel brick used in the burning zone of a cement rotary kiln and compared to the original brick. The results indicate that cement clinker and alkali salts are two important agents that cause corrosion especially of the bonding phase of refractory in cement rotary kilns.

The objective of this study is to correlate the infiltration resistance of magnesia-spinel refractory bricks made from different grades of magnesia by the clinker liquid phase, which is a gap in the literature about refractory bricks of magnesia-spinel.

2. Materials and methods

Two types of sintered magnesia (type 1 and 2) and an electrofused spinel were used. Raw materials were characterized regarding bulk density (BD) and apparent porosity (AP) according to the ABNT NBR 8592 standard. The chemical analysis was performed by X-ray fluorescence using a PW2540 Philips spectrometer, the X-ray diffraction analysis was performed using a PANalytical, model X'Pert PRO device, and the analysis was performed in the X'Pert HighSore Plus program using the JCPDS – International Centre for Diffraction Data as database. The Zeiss AXIO imager reflected light optical microscope was used to evaluate the microstructure of the sintered magnesia.

Table 1 shows the compositions of magnesia-spinel bricks produced in the laboratory. Thirty kilograms of each composition was mixed for 15 minutes on a roller mixer with the aid of an organic binder. Bricks of 160 mm x 85 mm x 64 mm in dimensions were pressed on a laboratory hydraulic press with pressure of approximately 150 MPa, which had passed through pre-drying at 120 °C for 12 hours, and oxidant firing at 1500 °C for 5 hours in a Bickley gas oven.

Composition	A-1	A-2
Sintered magnesia type 1	90%	-
Sintered magnesia type 2	-	90%
Electrofused spinel	10%	10%
Organic binder	3%	3%

Table 1
Composition of
magnesia-spinel bricks (wt.%).

After heat treatment, the bricks were characterized in relation to bulk density (BD) and apparent porosity (AP) according to the ABNT NBR 6220 standard; elasticity modulus at room temperature (EM) according to the ASTM C885 standard; cold crushing strength (CCS) according to the ABNT NBR 6224 standard; hot modulus of rupture (HMOR) at 1200 °C for 3 hours according to the ASTM C583 standard; abrasion according to the ASTM C704 and permeability according to the ASTM C577 standard. The infiltration test by clinker liquid phase was performed adopting a procedure similar to that of Kozuka (1993) testing, and was performed in a laboratory rotary kiln, as shown in Figure 1. The Kozuka testing was conducted at 1800 °C where 400 grams of clinker were added 5 times to the kiln, at an interval of 30 minutes, for a total addition of 2000 grams. After the test, the samples of 100 x 60 mm x 90 mm x 50 mm in a trapezoidal shape, were cut into 6 slices for chemical analysis, starting from the hot face (slice 1) to the cold face (slice 6).

Figure 1
Rotary kiln used in the infiltration test.

For the infiltration test, clinkers of three different cement factories (A, B and C) were collected. The clinkers were characterized using X-ray fluorescence and X-ray diffraction.

3. Results

Table 2 shows the properties of the raw materials used. The bulk density (BD), apparent porosity (PA) and chemical purity are different for the two types of magnesia. The magnesia type 1 showed lower BD and higher AP than type 2 and a typical microstructure shown in Figure 2, with a high content of elongated pores. Type 2 magnesia showed higher BD and lower AP than type 1 and a typical microstructure shown in Figure 3, with a reduced amount of pores. The bulk density of spinel is higher than the bulk density of magnesia due to the electrofusion process involving temperatures around 2000 °C.

Raw material	Magnesia type 1	Magnesia type 2	Electrofused spinel
BD (g/cm³)	2.95 ± 0.01	3.27 ± 0.00	3.42 ± 0.05
AP (%)	16.4 ± 0.2	3.7 ± 0.0	4.0 ± 1.0
Chemical analysis			
(Loss on ignition)	0.1	0.1	0.1
SiO_2	1.5	0.3	0.6
$Al2O_3$	0.4	0.1	63.4
Fe_2O_3	1.7	0.4	0.4
MnO	1.0	0.1	0.1
CaO	0.5	0.9	0.5
MgO	94.9	98.1	34.6
CaO/SiO_2 molar ratio	0.4	3.2	0.9
XRD	Periclase (MgO) Magnesium ferrite ($MgO.Fe_2O_3$) Monticellite ($CaO.MgO.SiO_2$) Forsterite ($2MgO.SiO_2$)	Periclase (MgO) Larnite (β $2CaO.SiO_2$)	Spinel ($MgO.Al_2O_3$) Periclase (MgO) Monticellite ($CaO.MgO.SiO_2$)

Table 2
Properties of the raw materials.

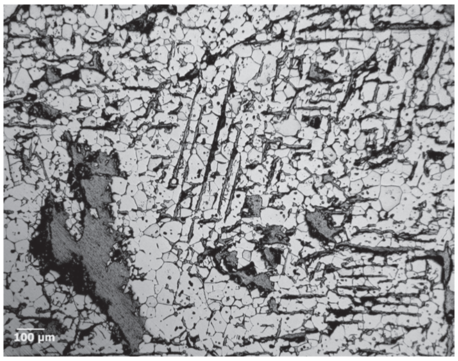

Figure 2
Microstruture of magnesia type 1.

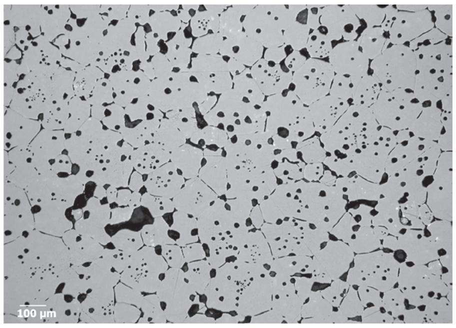

Figure 3
Microstructure of magnesia type 2.

Table 3 lists the properties of the compositions A-1 and A-2 after heat treatment at 1500 °C for 5 hours. All found properties were consistent with literature (Sczzerba et al., 2007; Rodríguez *et al*., 2013) and also with industrial production data. The composition A-2, produced with type 2 magnesia, exhibited superior properties than the composition A-1, with higher BD, CCS and HMOR and lower AP, abrasion and permeability.

Composition	A-1	A-2
BD (g/cm³)	2.85 ± 0.01	2.96 ± 0,00
AP (%)	19.4 ± 0.2	14.9 ± 0.1
EM (GPa)	33.0 ± 0.3	40.0 ± 0.4
CCS (MPa)	74 ± 3	81 ± 3
HMOR at 1200°C-3h (MPa)	10.8 ± 0.9	11.8 ± 0.8
Abrasion (cm³)	15 ± 2	12 ± 1
Permeabilility (cD)	27 ± 0	11 ± 1

Table 3
Properties of magnesia-spinel bricks.

The clinkers collected from three different cement factories (A, B and C) are characterized and results are shown in Table 4. The clinkers presented all of the clinker phases and similar contents of CaO, SiO_2, Al_2O_3 and Fe_2O_3, but the clinker collected in factory B showed the highest content of impurities such as K_2O and SO_3.

Clinker	A	B	C
(Loss on ignition)	0.2	0.2	0.2
SiO_2	21.0	21.2	21.6
$Al2O_3$	4.8	5.0	5.5
Fe_2O_3	3.8	2.2	3.3
CaO	65.4	67.0	66.5
MgO	2.6	1.0	0.6
Na_2O	0.2	0.0	0.1
K_2O	0.8	1.2	0.7
SO_3	0.9	1.6	1.0
XRD	C_3S βC_2S C_3A C_4AF	C_3S βC_2S C_3A C_4AF	C_3S βC_2S C_3A C_4AF

Table 4
Loss on ignition,
chemical composition (wt. %)
and phases identified by XRD of clinkers.

The results of the infiltration test by clinker liquid phase are shown in Figures 4 to 6 indicating the infiltration of CaO and SiO_2, which are the most relevant oxides, along the hot face (slice 1) to the cold face (slice 6) of the samples from A-1 and A-2 compositions. The composition A-1, produced with type 1 magnesia, showed the highest level of CaO and SiO_2 infiltration, independently of the clinker used in the test (A, B or C).

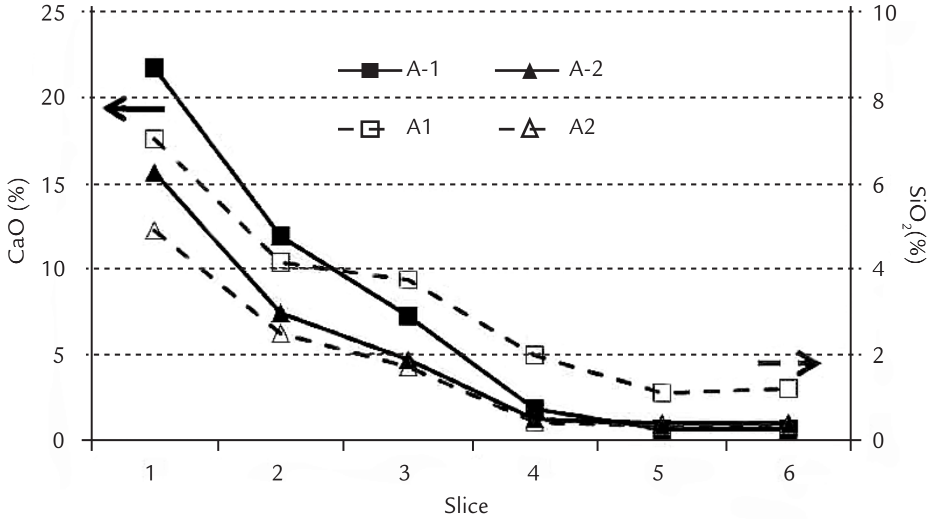

Figure 4
Infiltration of CaO e SiO_2 from the hot face (slice 1) to the cold face (slice 6) after infiltration test by clinker A.

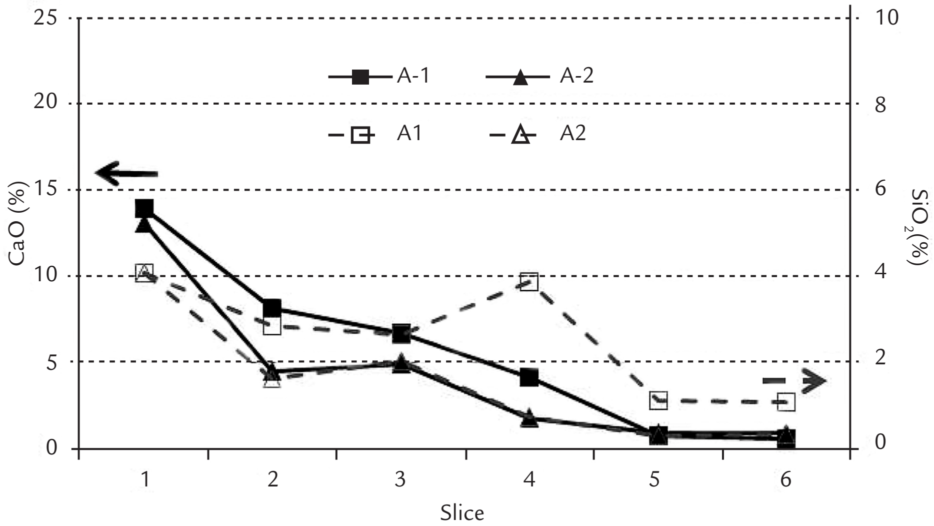

Figure 5
Infiltration of CaO e SiO_2 from the hot face (slice 1) to the cold face (slice 6) after infiltration test by clinker B.

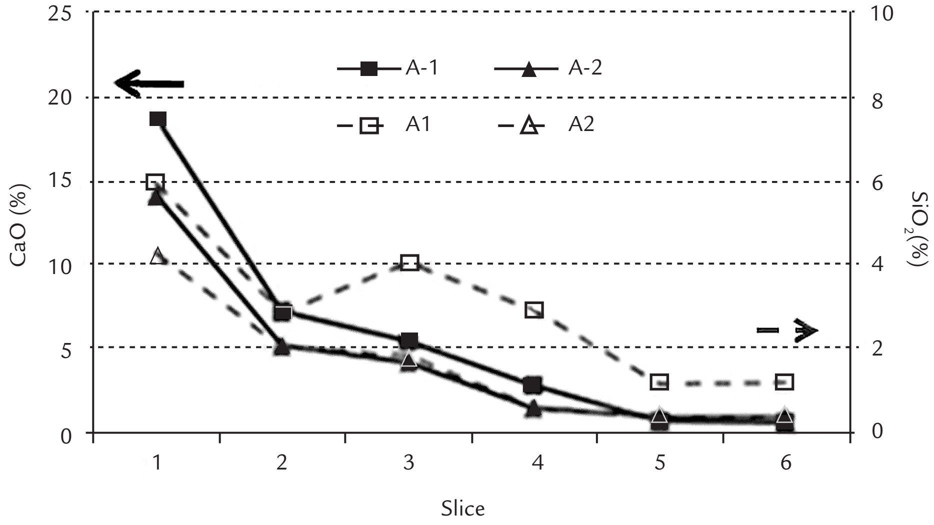

Figure 6
Infiltration of CaO and SiO_2 from the hot face (slice 1) to the cold face (slice 6) after infiltration test by clinker C.

4. Discussion

The chemical analysis of magnesia presented in Table 2 shows that the type 1 magnesia had a higher level of impurities (SiO_2, Fe2O_3 and MnO), with a lower MgO content in relation to the Type 2 magnesia. Due to the high content of SiO_2 of the Type 1 magnesia, the CaO/SiO_2 molar ratio has a value of 0.4 which determines the presence of minority phases such as forsterite (M_2S) and monticellite (CMS), besides magnesium ferrite (MF). The Type 2 magnesia shows the value of 3.2 for the CaO/SiO_2 molar ratio with the presence of minority phase larnite (βC2S) of high refractoriness.

The spinel composition is not stoichiometric (28.2 wt% MgO and 71.8 wt% Al_2O_3, Szczerba *et al.*, 2007), showing unreacted MgO. Excess of MgO is one way to ensure that there is no formation of *in situ* spinel during firing of magnesia-spinel bricks, since it is an expansive reaction (approximately 8% in volume), which may damage the mechanical strength of the refractory (Nakagama *et al.*, 1995).

Considering the transition zones of the cement rotary kiln, the superior characteristics of composition A-2, shown in Table 3, contribute to the better performance of the brick made with Type 2 magnesia. These results are in agreement with those obtained by Szczerba et al. (2007), who studied the influence of the physicochemical properties of magnesia on the final properties of magnesia-spinel products containing 8 or 18 wt% of electrofused spinel. Szczerba *et al.* (2007) reported that compositions containing sintered magnesia of high purity and superior physical properties achieved more suitable properties.

The results of the infiltration test of compositions A-1 and A-2 with clinkers A, B and C illustrate a classical phenomenon known as silicate migration. In steelmaking and non-ferrous industrial processes, due to the thermal gradient and operating conditions, the infiltration of slag rich in silicates (C_3S and C_2S) occurs in the open pores of the refractory, and this infiltration is more intense if the refractory contains a higher content of impurities, with formation of low refractoriness phases (Havranek, 1967).

The physicochemical properties of magnesia have a great influence on the properties and infiltration resistance of magnesia-spinel refractory bricks by the clinker liquid phase. Therefore, the use of high grade magnesia with a high purity, high bulk density and low apparent porosity leads to the production of magnesia-spinel bricks of high performance.

5. Conclusions

This investigation evaluated the influence of the physicochemical properties of magnesia on the properties and infiltration resistance of magnesia-spinel refractory bricks by the clinker liquid phase. The use of magnesia with low impurity content, presence of minority phase of high refractoriness, high bulk density and low apparent porosity improved properties and infiltration resistance. Therefore the use of high grade magnesia is essential for the production of high performance refractory.

6. References

AKSEL, C., RAND, B., RILEY, F.L., WARREN, P.D. Mechanical properties of magnesia-spinel composites. ***Journal of the European Ceramic Society***, v. 22, n. 5, p. 745-754, 2002.

AKSEL, C., WARREN, P.D., RILEY, F.L. Fracture behaviour of magnesia and magnesia–spinel composites before and after thermal shock. ***Journal of the European Ceramic Society,*** v. 24, n.8, p. 2407-2416, 2004a.

AKSEL, C., RAND, B., RILEY, F.L., WARREN, P.D. Thermal shock behaviour of magnesia–spinel composites. ***Journal of the European Ceramic Society,*** v. 24, n. 9, p. 2839-2845, 2004b.

AKSEL, C., WARREN, P.D, RILEY, F.L. Magnesia–spinel microcomposites. ***Journal of the European Ceramic Society,*** v. 24, n. 10–11, p. 3119-3128, 2004c.

GHOSH, A., SARKAR, R., MUKHERJEE, B., DAS, S.K. Effect of spinel content on the properties of magnesia–spinel composite refractory. ***Journal of the European Ceramic Society,*** v. 24, n.7, p.2079-2085, 2004.

GONÇALVES, G.E, BITTENCOURT, L.R.M. The mechanisms of formation of mayenite (C12A7) and the quaternary phase Q (Ca20Al26Mg3Si3O68) of the system $CaO\text{-}MgO\text{-}Al_2O_3\text{-}SiO_2$ in magnesia-spinel bricks used in the burning and transition zones of rotary cement kilns. In: UNITECR'03, 03, 2003. Proceedings….Osaka: Technical Association of Refractories, 2003. p.138-141.

GRASSET-BOURDEL, R., ALZINA, A., HUGER, M., GRUBER, D., HARMUTH, H., CHOTARD, T. Influence of thermal damage occurrence at microstructural scale on the thermomechanical behaviour of magnesia–spinel refractories. ***Journal of the European Ceramic Society,*** v. 32, n.5, p. 989-999, 2012.

GRASSET-BOURDEL, R., ALZINA, A., HUGER, M., CHOTARD, T., EMLER, R., GRUBER, D., HARMUTH, H. Tensile behaviour of magnesia-spinel refractories: Comparison of tensile and wedge splitting tests. ***Journal of the European Ceramic Society,*** v. 33, n. 5, p. 913-923, 2013.

HAVRANEK, P.H, DAVIES, B. Diffusion of open hearth slags in basic refractories. ***Ceramic Bulletin***, v.46, n.5, p. 534-538, 1967.

KOZUKA, H. et al. New kind of chrome-free (MgO-CaO-ZrO2) bricks for burning zone of rotary cement kiln. In: UNITECR'93, 1993. Proceedings… São Paulo: Technical Association of Refractories, 1993. p.1027-1037.

LIU, G., LI J., CHEN K. Combustion synthesis of refractory and hard materials: a review. ***International Journal of Refractory Metals and Hard Materials,*** v. 39, p. 90-102, 2013.

LIU, G., LI, N., YAN, W., GAO, C., ZHOU, W., LI, Y. Composition and microstructure of a periclase–composite spinel brick used in the burning zone of a cement rotary kiln. ***Ceramics International***, v. 40, p. 8149-8155, 2014.

MOURÃO, M. B. et alii. Introdução à Siderurgia. São Paulo:ABM, 2007.

NAKAGAMA, Z. et al. Effect of corundum/periclase sizes on expansion behavior during synthesis of spinel. In: UNITECR'95, 1995. Proceedings... Kyoto: Technical Association of Refractories, 1995. p. 379-386.

RODRÍGUEZ, E., CASTILLO, G.A., CONTRERAS, J., PUENTE-ORNELAS, R., AGUILAR-MARTÍNEZ, J.A, GARCÍA, L., GÓMEZ, C. Hercynite and magnesium aluminate spinels acting as a ceramic bonding in an electrofused MgO–$CaZrO_3$ refractory brick for the cement industry. ***Ceramics International,*** v. 38, p. 6769-6775, 2012.

RODRÍGUEZ, E.A., CASTILLO, G.A., DAS, T.K., PUENTE-ORNELAS, R., GONZÁLEZ, Y., ARATO, A.M., AGUILAR-MARTÍNEZ, J.A. MgAl2O4 spinel as an effective ceramic bonding in a MgO–$CaZrO_3$ refractory. ***Journal of the European Ceramic Society,*** v. 33, n. 13–14, p. 2767-2774, 2013.

SARKAR, R., GHOSH, A., DAS, S.K. Reaction sintered magnesia rich magnesium aluminate spinel: effect of alumina reactivity. ***Ceramics International,*** v. 29, n. 4, p. 407-411, 2003.

SZCZERBA, J., PĘDZICH, Z., NIKIEL M., KAPUŚCIŃSKA D. Influence of raw materials morphology on properties of magnesia-spinel refractories. ***Journal of the European Ceramic Society.*** v. 27, p.1683-1689, 2007.

TAYLOR, HFW. ***Cement chemistry.*** London: Academic Press, 1990.

WAJDOWICZ, A.A. et al. Magnesia-spinel brick: a thermal overload case. In: ECREF European Centre for Refractories, 54, 2011. Proceedings... Aachen: ECREF European Centre for Refractories, 2011. p. 2-5.

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